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(54) Title: SALINE SOLUBLE INORGANIC FIBRES

(57) Abstract

The use of P_2O_5 and/or B_2O_3 as a component to improve the refractoriness of inorganic fibres comprising SiO_2, and CaO and/or MgO is described. The inorganic fibres have a composition such that $SiO_2 + P_2O_5$-(58 + (if MgO > 10, 0.5 x (MgO-10) else 0)) > -2.4 wt.%.

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SALINE SOLUBLE INORGANIC FIBRES

This invention relates to saline soluble inorganic fibres.

Saline soluble inorganic fibres have been described in several patent specifications, see for example WO93/15028. Fibres are required to be soluble in saline solution so that inhaled or ingested fibres dissolve rather than providing a source of irritation or otherwise affecting health. WO93/15028 showed that fibres comprising SiO_2, CaO and MgO and having a silica content of greater than 58% (or greater than 58% plus 0.5 times (wt%MgO - 10) if MgO > 10wt%) had suitable shrinkage characteristics at 800°C and 1000°C to be usable as refractory materials. A further feature of WO93/15028 was the use of the percentage of non-bridging oxygens present to predict the solubility of fibres in physiological saline solution.

Various subsequent applications have described the effect of P_2O_5 and B_2O_3 on solubility - see for example WO95/29135. P_2O_5 is alleged to have a solubilising effect on such fibres.

The German government have proposed a fibre classification which turns on a variable K_I which is defined as:

$$K_I = \Sigma(\text{Na,K,B,Ca,Mg,Ba -oxide}) - 2^* \text{Al-oxide}$$

(the amounts of the oxides being expressed as weight %)

According to the proposed fibre classification if K_I is greater than 40 the fibre requires no health warnings. If K_I lies between 30 and 40 the fibre requires health warnings to be made. If K_I is less than 30 more serious marking is required (it is labelled as a carcinogen). It is readily apparent that it is difficult to provide a high K_I fibre (K_I>40) while still providing a refractory fibre like that of WO93/15028 (SiO_2>58wt%), there being a very narrow window of compositions to meet.

As a result of investigating fibre compositions that may meet the fibre classification and yet still be refractory enough to meet the standard of WO93/15028 (shrinkage of less than 3.5% at both 800°C and1000°C) the applicants have found that addition of P_2O_5 to compositions allows a broader range of refractory fibres to be produced than had previously been appreciated. They have also found that B_2O_3, previously thought to be

extremely detrimental to refractoriness, has a similar, although lesser, effect and that both P_2O_5 and B_2O_3 may be used in the fibres of WO93/15028.

The applicants have found that the refractoriness of the P_2O_5 and B_2O_3 containing fibres of the present invention is dependent on the sum of the amounts of SiO_2 and P_2O_5 (expressed in wt%)

It appears that a further factor that may be important in determining the refractoriness of a fibre is the percentage of non-bridging oxygens.. If this percentage is 61.4% or more (calculated on the basis of the amounts of the components SiO_2, CaO, MgO, P_2O_5, and B_2O_3) the fibres tend to fail shrinkage tests at 800°C and 1000°C (failure being defined as a shrinkage of 3.5% or more).

Accordingly the present invention provides the use of P_2O_5 and/or B_2O_3 as a component to improve the refractoriness of inorganic fibres comprising SiO_2, and CaO and/or MgO, the inorganic fibres having a composition such that

$$SiO_2 + P_2O_5 - (58 + (\text{if } MgO > 10,\ 0.5 \times (MgO - 10) \text{ else } 0)) > -2.4 \text{wt\%}$$

The invention provides further such fibres in which the percentage of non-bridging oxygens is less than 61.4%.

Further features of the invention are apparent from the claims in the light of the following description.

The percentage of non-bridging oxygens (%N.B.O.) is calculated by converting the weight percentages of SiO_2, CaO, MgO, P_2O_5, and B_2O_3 to molar amounts and inserting these amounts into the equation:-

$$\%N.B.O. = \frac{2 * (CaO + MgO + P_2O_5 + B_2O_3)}{(2 * SiO_2 + CaO + MgO + 5 \times P_2O_5 + 3 \times B_2O_3)} \times 100$$

The reason the amounts of CaO, MgO, P_2O_5, and B_2O_3 are doubled in the numerator to this equation is that each contributes two non-bridging oxygens. The reason terms are multiplied in the denominator to this equation is to reflect the number of oxygen atoms each molecular formula possesses.

Table I shows the results of a first set of shrinkage and solubility tests on compositions comprising SiO_2, CaO, MgO, P_2O_5, and B_2O_3 as main

ingredients. In this table the analysed compositions are normalised to 100%. It is clear from these compositions that where the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is greater than 61.4% (those fibres lying above line A of Table I) the fibres fail the shrinkage tests, having shrinkages of greater than 3.5% at either or both of 800°C and 1000°C.

WO93/15028 stressed the importance of alumina content and the fibres lying between lines B and A of Table I show that alumina contents of greater than 1wt% are damaging to the shrinkage properties of fibres.

The applicants have also found that the combined amount of CaO and MgO is important. Those fibres lying between lines C and B have a combined CaO and MgO content of greater than 42wt% and also fail the shrinkage tests.

The fibres below line C have a percentage of non-bridging oxygens less than 61.4%, an alumina content of less than 1wt%, and a combined CaO and MgO content of less than 42wt%. All of these fibres pass the shrinkage tests. These fibres fall within the compositional ranges:-

SiO_2	52.4 - 57.85wt%
CaO	22.2 - 39.4wt%
MgO	1.96 - 17.4wt%
P_2O_5	0.82 - 7.8wt%
B_2O_3	0 - 1.95wt%
Al_2O_3	<1wt%

The solubility results presented in Table I were obtained by the methods described in WO93/15028 and show a high solubility for all of the fibres produced.
It can be seen that all of the fibres below line C have a K_I of more than 35 and more than half have a K_I of more than 40.

Further testing resulted in the data presented in Table II. The data presented are as in table I but an additional column entitled deviation shows the result of looking to the difference between the sum of the SiO_2 and P_2O_5 contents and the SiO_2 amount predicted to be needed by WO93/15028 for a fibre to be refractory (shrinkage of less than 3.5% at both 800°C and 1000°C. The figure given is found by calculating the sum

$SiO_2 + P_2O_5 - (58 + (\text{if } MgO > 10,\ 0.5 \times (MgO - 10) \text{ else } 0))$

If this is less than -2.4wt% the fibres fail. The fibres that failed are shown in plain text, those that passed in bold text, and those that were difficult to form in italics.

More than 12.5wt% P_2O_5 is undesirable as it causes difficulties in making the fibres.

While the above description and the claims refer to P_2O_5, B_2O_3, SiO_2, CaO and MgO it will be clear to the person skilled in the art that the pure materials need not be used and that provision of these components in combined form (e.g. provision of P_2O_5 in the form of mixed oxide phosphates) is part of the invention.

Table I

Code	Chemical Composition (XRF - Weight percent)											KI	Shrinkage		Solubility (ppm)						% N.B.O.	
LTP	CaO	MgO	P2O5	SiO2	Al2O3	Na2O	K2O	B2O3	Fe2O3	ZrO2	SrO		800°C	1000°C	CaO	MgO	SiO2	B2O3	Total	CaO+MgO		
LTP 8	24.95	19.18	3.41	51.69	0.25	0.30	0.05		0.17	< 0.05	< 0.05	44.0	40.0	40.0	53	98	177		328	44.14	68.5%	
LTP 9	24.81	18.66	5.10	50.42	0.38	0.31	<0.05		0.17	0.15	< 0.05	43.0	23.9	38.8	59	115	193		367	43.47	68.1%	
LTP11	25.13	19.07	2.51	52.54	0.28	0.25	0.05		0.17	< 0.05	< 0.05	43.9	46.8	39.1	55	94	174		323	44.20	68.0%	
LTP16	31.83	12.27	3.39	51.59	0.26	0.42	0.06		0.17	< 0.05	< 0.05	44.1	49.1		79	76	200		355	44.11	66.1%	
LTP10	24.48	17.89	2.48	54.46	0.21	0.28	0.05		0.16	< 0.05	< 0.05	42.3	3.62	19.1	58	90	169		317	42.37	64.7%	
LTP 4	24.04	17.78	3.31	53.85	0.31	0.26	0.05		0.15	0.25	< 0.05	41.5	3.71	4.77	56	95	180		331	41.83	64.3%	
LTP 5	24.22	17.17	4.91	52.72	0.33	0.30	< 0.05		0.14	0.21	< 0.05	41.0	3.63	5.39	65	106	191		362	41.40	64.1%	
LTP17	38.39	5.54	3.41	51.22	0.40	0.42	0.07		0.16	0.38	< 0.05	43.6	45.2	43.8	83	32	191		306	43.94	63.9%	
LTP23	38.62	5.56	2.57	52.23	0.34	0.46	0.07		0.15	< 0.05	< 0.05	44.0	42.90		82	29	199		310	44.18	63.7%	
LTP14	30.93	11.01	4.90	51.96	0.30	0.45	0.05		0.15	0.25	< 0.05	41.8	3.24	3.92	78	69	191		338	41.95	63.0%	
LTP13	11.28	27.95	3.26	57.2	< 0.05	0.13	< 0.05		0.17	< 0.05	< 0.05	39.4	5.72	5.26	30	117	188		335	39.23	63.0%	
LTP12	30.93	11.35	3.36	53.52	0.32	0.31	0.06		0.15	< 0.05	< 0.05	42.0	2.55	30.1	82	72	207		361	42.27	62.6%	
LTP20	31.05	11.35	2.52	54.14	0.32	0.31	0.06		0.16	0.10	< 0.05	42.1	3.38	29.7	85	71	200		356	42.40	62.6%	
LTP15	36 89	5.70	5.05	51.22	0.31	0.43	0.10		0.16	0.13	< 0.05	42.5	3.41	5.03	88	35	204		327	42.59	62.2%	
LTP 3	22.89	16.69	6.70	52.58	0.25	0.29	< 0.05		0.14	0.46	< 0.05	39.4	23.3	29.5	43	166	141		350	39 58	61.9%	
LTP 7	10.37	27.85	3.29	58.18	< 0.05	0.15	< 0.05		0.16	< 0.05	< 0.05	38.4	10.9	15.5	36	132	152		320	38.23	61.4%	A
LTP52	24.9	11.5	4.89	54.8	2.06	0.28	0.05	<0.05	1.38	<0.05	<0.05	32.6	32.1		72	74	140		286	36.40	56.0%	
LTP51	28.7	11	1.62	56.6	1.38	0.29	0.07	<0.05	0.26	<0.05	<0.05	37.3	3.07	3.61	82	69	159		310	39.70	58.4%	B
LTP29	40.29	2.09	1.23	55.09	0.43	0.39	0.12		0.19	0.17	< 0.05	42.0	45.9		76	10	206		292	42.38	58.8%	
LTP21	36.62	5.58	2.54	54.19	0.39	0.46	0.07		0.15	< 0.05	< 0.05	42.0		35.5	58	34	208		300	42.20	60.3%	C
LTP30	39.40	1.96	2.22	55.25	0.45	0.41	0.10		0.21	<0.05	< 0.05	41.0	1.74	2.04	72	11	209		292	41.36	57.5%	
LTP41	31.36	9.48	0.85	55.63	0.27	0.30	0.07	1.88	0.16	<0.05	< 0.05	42.5	1.20	2.32	87	60	194	20	361	40.84	60.0%	
LTP 6	29.83	10.45	3.34	55.65	0.21	0.32	0.05		0.15	< 0.05	< 0.05	40.2	1.89	2.76	65	52	172		289	40.28	59.0%	
LTP34	30.44	9.81	1.68	57.3	0.25	0.31	0.07		0.15	<0.05	< 0.05	40.1	1.40	1.79	76	51	188		315	40.25	58.0%	
LTP43	30.51	9.68	1.68	56.19	0.28	0.32	0.07	1.11	0.15	<0.05	< 0.05	41.1	0.97	1.84	62	66	187	12	327	40.19	58.8%	
LTP42	30.55	9.56	0.86	57.13	0.27	0.33	0.07	1.08	0.15	<0.05	< 0.05	41.1	1.04	1.81	75	65	192	12	344	40.12	58.2%	
LTP47	22.2	17.4	3.98	55.2	0.31	0.31	0.05	<0.05	0.1	<0.05	<0.05	39.3	1.97	2.14	58	104	197		359	39.60	61.0%	
LTP38	34.82	4.73	0.82	57.84	0.31	0.30	0.08	0.94	0.15	<0.05	< 0.05	40.3	1.07	1.40	83	25	175	9	292	39.56	55.4%	
LTP 2	23.35	16.10	4.87	54.25	0.46	0.24	< 0.05		0.16	0.58	< 0.05	38.8	2.24	3.05	53	96	167		316	39.45	60.8%	
LTP39	34.35	4.73	1.67	57.39	0.27	0.30	0.08	1.06	0.14	<0.05	< 0.05	40.0	1.47	1.93	32	33	203	16	284	39.08	55.2%	
LTP 1	23.29	15.66	3.33	57.01	0.24	0.22	0.06		0.14	< 0.05	0.05	38.7	1.31	1.77	63	89	175		327	38.94	58.7%	
LTP48	32	6.87	7.8	52.4	0.52	0.34	0.05	<0.05	0.15	0.18	<0.05	38.2	1.24	1.53	84	48	205		337	38.87	57.7%	
LTP40	33.67	4.75	0.86	57.85	0.38	0.31	0.08	1.95	0.15	<0.05	< 0.05	40.0	1.15	2.39	40	32	194	25	291	38.42	54.5%	
LTP26	33.69	4.56	3.73	56.95	0.36	0.43	0.06		0.14	0.07	< 0.05	38.0	1.22	1.40	91	28	193		312	38.25	54.0%	
LTP27	28.91	9.33	3.66	57.32	0.22	0.36	0.05		0.14	<0.05	< 0.05	38.2	0.99	1.16	67	48	173		288	38.24	55.5%	
LTP46	28.4	8.69	2.67	59	0.29	0.33	0.06	<0.05	0.13	<0.05	<0.05	36.9	0.91	0.99	71	46	175		292	37.09	53.3%	

TABLE II (Part 1)

Code	Chemical Composition (XRF - Weight percent)											KI	Shrinkage			Solubility (ppm)						% N.B.O.
LTP	CaO	MgO	P2O5	SiO2	Al2O3	Na2O	K2O	B2O3	Fe2O3	ZrO2	SrO		800°C	1000°C	Deviation	CaO	MgO	SiO2	B2O3	Total	CaO+MgO	
LTP 8	24.95	19.18	3.41	51.69	0.25	0.30	0.05		0.17			43.99	40.00	40.00	-7.49	53	98	177		328	44.14	68.5%
LTP11	25.13	19.07	2.51	52.54	0.28	0.25	0.05		0.17			43.94	46.80	39.10	-7.48	55	94	174		323	44.20	68.0%
LTP49	32.35	6.74		50.54	0.57	0.40	0.08	9.17	0.14			47.60	2.65	15.70	-7.46	79	41	214	129	463	39.09	62.1%
LTP 9	24.81	18.66	5.10	50.42	0.38	0.31			0.17	0.15		43.03	23.90	38.80	-6.81	59	115	193		367	43.47	68.1%
LTP67	15.17	25.18	5.06	54.00	0.19	0.25			0.15			40.22	5.70	-	-6.53						40.35	64.9%
LTP13	11.28	27.95	3.26	57.20		0.13			0.17			39.36	5.72	5.26	-6.51	30	117	188		335	39.23	63.0%
LTP62	14.99	24.54	2.52	57.24	0.35	0.19			0.16			39.02	4.48	-	-5.51	25	66	119		210	39.53	62.3%
LTP 7	10.37	27.85	3.29	58.18		0.15			0.16			38.37	10.90	15.50	-5.46	36	132	152		320	38.23	61.4%
LTP10	24.48	17.89	2.48	54.46	0.21	0.28	0.05		0.16			42.28	3.62	19.10	-5.01	58	90	169		317	42.37	64.7%
LTP 4	24.04	17.78	3.31	53.85	0.31	0.26	0.05		0.15	0.25		41.52	3.71	4.77	-4.73	56	95	180		331	41.83	64.3%
LTP16	31.83	12.27	3.39	51.59	0.26	0.42	0.06		0.17			44.07	49.10	-	-4.15	79	76	200		355	44.11	66.1%
LTP 5	24.22	17.17	4.91	52.72	0.33	0.30			0.14	0.21		41.04	3.63	5.39	-3.96	65	106	191		362	41.40	64.1%
LTP59	32.13	10.47	12.93	41.37	2.31	0.56	0.05		0.17			38.59	43.20	-	-3.94	42	41	179		262	42.60	69.3%
LTP50	31.00	10.40		54.50	0.36	0.31	0.08	3.19	0.16			44.26	29.80	-	-3.70	79	58	200	30	367	41.40	62.0%
LTP17	38.39	5.54	3.41	51.22	0.40	0.42	0.07		0.16	0.38		43.62	45.20	43.80	-3.37	83	32	191		306	43.94	63.9%
LTP56	34.38	9.46	14.72	40.02	0.72	0.55			0.16			42.95	9.98	-	-3.26	60	57	196		313	43.84	70.5%
LTP23	38.62	5.56	2.57	52.23	0.34	0.46	0.07		0.15			44.03	42.90	-	-3.20	82	29	199		310	44.18	63.7%
LTP57	*34.73*	*9.55*	*19.83*	*35.24*	*0.23*	*0.26*			*0.15*			*44.08*	-	-	*-2.93*					*0*	*44.28*	*73.0%*
LTP70	24.38	14.20		57.52	0.44	0.18	0.08	3.01	0.18			40.97	3.63	7.86	-2.58	75	73	255	21	424	38.58	58.7%
LTP63	14.61	22.87	2.53	59.45	0.27	0.12			0.16			37.06	9.57	-	-2.46	17	108	83		208	37.48	58.4%
Above here compositions have deviation of more than 2.4wt%																						
LTP54	*29.40*	*8.73*	*14.55*	*46.68*	*0.07*	*0.44*			*0.13*			*38.43*	-	-	*3.23*						*38.13*	*60.1%*
LTP61	32.46	9.86	14.02	42.67	0.09	0.70	0.05		0.15			42.89	3.44	3.65	-1.31						42.32	67.4%
LTP60	*31.46*	*9.58*	*12.64*	*44.91*	*0.69*	*0.54*	*0.05*		*0.14*			*40.25*	-	-	*-0.45*						*41.04*	*64.8%*
Above here compositions have P2O5 content more than 12.5wt%																						
LTP52	24.93	11.52	4.90	54.88	2.06	0.28	0.05		1.38			32.66	32.10	-	1.02	72	74	140		286	36.45	56.1%
LTP51	28.72	11.01	1.62	56.65	1.38	0.29	0.07		0.26			37.33	3.07	3.61	-0.24	82	69	159		310	39.73	58.4%
Above here fibres have Al2O3 content above 1 wt%																						
LTP15	36.89	5.70	5.05	51.22	0.31	0.43	0.10		0.16	0.13		42.50	3.41	5.03	-1.72	88	35	204		327	42.59	62.2%
LTP14	30.93	11.01	4.90	51.96	0.30	0.45	0.05		0.15	0.25		41.85	3.24	3.92	-1.65	78	69	191		338	41.95	63.0%
LTP58	32.93	9.77	12.01	44.34	0.19	0.53	0.05		0.19			42.98	2.62	2.78	-1.65	57	42	223		322	42.70	67.0%
LTP55	32.58	9.47	9.65	46.79	0.84	0.46	0.05		0.17			40.88	1.72	1.95	-1.56	71	54	203		328	42.05	65.1%
LTP53	29.34	9.84	9.58	50.26	0.17	0.56	0.05		0.15	0.05		39.45	0.01	0.00	1.84	71	83	222		376	39.18	60.1%
Above here SiO2 content less than 52wt%																						

TABLE II (Part 2)

Code	Chemical Composition (XRF - Weight percent)											KI	Shrinkage			Solubility (ppm)						% N.B.O.
I.TP	CaO	MgO	P2O5	SiO2	Al2O3	Na2O	K2O	B2O3	Fe2O3	ZrO2	SrO		800°C	1000°C	Deviation	CaO	MgO	SiO2	B2O3	Total	CaO+MgO	
I.TP 3	22.89	16.69	6.70	52.58	0.25	0.29			0.14	0.46		39.37	23.30	29.50	-2.07	43	166	141		350	39.58	61.9%
I.TP20	31.05	11.35	2.52	54.14	0.32	0.31	0.06		0.16	0.10		42.13	3.38	29.70	-2.01	85	71	200		356	42.40	62.6%
I.TP 2	23.35	16.10	4.87	54.25	0.46	0.24			0.16	0.58		38.77	2.24	3.05	-1.93	53	96	167		316	39.45	60.8%
I.TP12	30.93	11.35	3.36	53.52	0.32	0.31	0.06		0.15			42.00	2.55	30.10	-1.79	82	72	207		361	42.27	62.6%
I.TP21	36.62	5.58	2.54	54.19	0.39	0.46	0.07		0.15			41.95	-	35.50	-1.27	58	34	208		300	42.20	60.3%
I.TP48	31.90	6.85	7.78	52.24	0.52	0.34	0.05		0.15	0.18		38.10	1.24	1.53	2.02	84	48	205		337	38.75	57.7%
Above here SiO2 content 52wt% to less than 55wt%																						
I.TP47	22.30	17.48	4.00	55.45	0.31	0.31	0.05		0.10			39.52	1.97	2.14	-2.29	58	104	197		359	39.78	61.0%
I.TP64	20.81	18.41	2.52	57.63	0.22	0.26			0.14			39.04	3.01	3.73	-2.05	46	76	197		319	39.22	59.7%
LTP68	20.08	18.77	4.55	55.92	0.30	0.24			0.14			38.49	3.90	4.16	-1.92	51	89	226		366	38.85	60.2%
LTP29	40.29	2.09	1.23	55.09	0.43	0.39	0.12		0.19	0.17		42.03	45.85	-	-1.68	76	10	206		292	42.38	58.8%
I.TP41	31.36	9.48	0.85	55.63	0.27	0.30	0.07	1.88	0.16			42.55	1.20	2.32	-1.52	87	60	194	20	361	40.84	60.0%
I.TP71	38.31	0.65		56.51	0.55	0.20	0.09	3.54	0.14			41.69	0.59	1.43	-1.49	73	2	278	55	408	38.96	54.9%
LTP30	39.40	1.96	2.22	55.25	0.45	0.41	0.10		0.21			40.96	1.74	2.04	-0.53	72	11	209		292	41.36	57.5%
LTP 1	23.29	15.66	3.33	57.01	0.24	0.22	0.06		0.14		0.05	38.74	1.31	1.77	-0.49	63	89	175		327	38.94	58.7%
I.TP43	30.51	9.68	1.68	56.19	0.28	0.32	0.07	1.11	0.15			41.13	0.97	1.84	-0.12	62	66	187	12	327	40.19	58.8%
I.TP37	35.40	4.77		57.92	0.31	0.31	0.09	1.05	0.15			40.99	1.57	2.13	-0.08	37	30	195	13	275	40.16	56.1%
I.TP32	30.01	8.53		57.95	0.32	0.23	0.09	2.69	0.18			40.92	1.68	2.83	-0.05	80	46	184	24	334	38.54	56.3%
I.TP73	36.93	0.62		57.96	0.49	0.23	0.09	3.54	0.13			40.43	1.23	3.00	-0.04	76	2	264	40	382	37.55	52.6%
I.TP42	30.55	9.56	0.86	57.13	0.27	0.33	0.07	1.08	0.15			41.06	1.04	1.81	-0.02	75	65	192	12	344	40.12	58.2%
LTP38	34.82	4.73	0.82	57.84	0.31	0.30	0.08	0.94	0.15			40.26	1.07	1.40	0.66	83	25	175	9	292	39.56	55.4%
LTP40	33.67	4.75	0.86	57.85	0.38	0.31	0.08	1.95	0.15			40.00	1.15	2.39	0.71	40	32	194	25	291	38.42	54.5%
I.TP 6	29.83	10.45	3.34	55.65	0.21	0.32	0.05		0.15			40.23	1.89	2.76	0.76	65	52	172		289	40.28	59.0%
I.TP69	19.17	17.56	4.66	57.93	0.31	0.23			0.13			36.34	1.23	1.68	0.81	49	88	241		378	36.73	56.5%
I.TP34	30.44	9.81	1.68	57.30	0.25	0.31	0.07		0.15			40.13	1.40	1.79	0.98	76	51	188		315	40.25	58.0%
I.TP39	34.35	4.73	1.67	57.39	0.27	0.30	0.08	1.06	0.14			39.98	1.47	1.93	1.06	32	33	203	16	284	39.08	55.2%
I.TP26	33.69	4.56	3.73	56.95	0.36	0.43	0.06		0.14	0.07		38.02	1.22	1.40	2.68	91	28	193		312	38.25	54.0%
I.TP27	28.91	9.33	3.66	57.32	0.22	0.36	0.05		0.14			38.21	0.99	1.16	2.99	67	48	173		288	38.24	55.5%
Above here SiO2 content 55wt% to less than 58wt%																						

TABLE II (Part 3)

Code	Chemical Composition (XRF - Weight percent)											KI	Shrinkage			Solubility (ppm)						
LTP	CaO	MgO	P2O5	SiO2	Al2O3	Na2O	K2O	B2O3	Fe2O3	ZrO2	SrO		800°C	1000°C	Deviation	CaO	MgO	SiO2	B2O3	Total	CaO+MgO	% N.B.O.
LTP66	15.65	21.16	4.38	58.17	0.24	0.25			0.15			36.58	2.65	3.19	-1.03	30	84	169		283	36.81	57.7%
LTP65	20.36	17.74	2.50	58.75	0.30	0.22			0.13			37.72	2.28	2.37	-0.62	41	68	185		294	38.10	57.6%
LTP72	22.67	13.60		59.64	0.37	0.27	0.06	3.25	0.14			39.11	3.37	6.16	-0.16	49	56	197	23	325	36.27	55.0%
LTP35	32.72	4.76		58.60	0.28	0.31	0.08	3.09	0.15			40.40	1.65	3.85	0.60	88	26	179	29	322	37.48	53.5%
LTP31	28.30	9.20		58.70	0.28	0.29	0.06	3.00	0.18			40.29	3.15	4.88	0.70	91	60	205	31	387	37.50	55.1%
LTP36	33.37	4.82		58.98	0.27	0.30	0.08	2.10	0.15			40.13	1.50	3.12	0.90	37	33	198	25	293	38.19	53.9%
LTP33	30.20	9.03		59.01	0.27	0.28	0.08	0.96	0.17			40.02	2.16	2.74	1.01	88	52	193	18	343	39.23	56.1%
LTP44	29.05	6.88		59.81	0.35	0.36	0.07	3.16	0.13		0.19	38.82	1.60	2.71	1.81	89	44	193	32	358	35.93	52.1%
LTP45	24.10	11.48		62.48	0.54	0.24	0.06	1.04	0.15			35.76	2.17	3.15	3.78	81	65	189	10	345	35.50	51.3%
LTP46	28.52	8.73	2.68	59.25	0.29	0.33	0.06		0.13			37.06	0.91	0.99	3.93	71	46	175		292	37.25	53.3%

Above here SiO2 content 58wt% or more

CLAIMS

1. The use of P_2O_5 or B_2O_3 as a component to improve the refractoriness of inorganic fibres comprising SiO_2, and CaO and/or MgO, to produce inorganic fibres having a composition having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours, the fibres having a composition such that

$$SiO_2 + P_2O_5 - (58 + (\text{if } MgO > 10,\ 0.5 \times (MgO - 10) \text{ else } 0)) > -2.4\text{wt\%}$$

2. The use of P_2O_5 or B_2O_3 as a component to improve the refractoriness of inorganic fibres as claimed in claim 1 in which the percentage of non-bridging oxygens is less than 61.4%.

3. The use of P_2O_5 or B_2O_3 as a component to improve the refractoriness of inorganic fibres as claimed in claim 1 or claim 2 in which the fibres fall within the compositional range:-

SiO_2	44 or more
CaO	20 - 40wt%
MgO	0 - 18wt%
P_2O_5	0- 12.5wt%
B_2O_3	0 - 4wt%

4. The use of P_2O_5 or B_2O_3 as a component to improve the refractoriness of inorganic fibres as claimed in claim 3 in which the fibres fall within the compositional range:-

SiO_2	52 - <58wt% [52 - <58+0.5´(MgO-10)wt% if MgO > 10wt%]
CaO	22 - 40wt%
MgO	0 - 17.5wt%
MgO + CaO	< 42wt%
P_2O_5	0.5 - 10wt%
B_2O_3	0 - 2wt%

5. The use of P_2O_5 or B_2O_3 as a component to improve the refractoriness of inorganic fibres as claimed in claim 3 in which the fibres fall within the compositional range:-

SiO_2	44.34 - 62.48

CaO	20.36 - 39.4wt%
MgO	0.62 - 21.16wt%
P_2O_5	0 - 12.01wt%
B_2O_3	0 - 3.54wt%

6. Saline soluble inorganic fibres having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours, in which:-

$$SiO_2 + P_2O_5 - (58 + (\text{if MgO} > 10,\ 0.5 \times (\text{MgO} - 10)\ \text{else}\ 0)) > -2.4\text{wt\%}$$

7. Saline soluble inorganic fibres as claimed in claim 6 comprising:-

SiO_2	44 or more
CaO	20 - 40wt%
MgO	0 - 18wt%
P_2O_5	0- 12.5wt%
B_2O_3	0 - 4wt%

8. Saline soluble inorganic fibres as claimed in claim 7 comprising:-

SiO_2	52 - <58wt% [52 - <58+0.5'(MgO-10)wt% if MgO > 10wt%]
CaO	22 - 40wt%
MgO	0 - 17.5wt%
MgO + CaO	< 42wt%
P_2O_5	0.5 - 10wt%
B_2O_3	0 - 2wt%

and in which the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is less than 61.4%.

9. Saline soluble inorganic fibres as claimed in claim 7 comprising:-

SiO_2	44.34 - 62.48
CaO	20.36 - 39.4wt%
MgO	0.62 - 21.16wt%
P_2O_5	0 - 12.01wt%
B_2O_3	0 - 3.54wt%

10. Saline soluble inorganic fibres as claimed in claim 6 in which the fibres have a composition:-

SiO_2	52.4 - 57.85wt%
CaO	22.2 - 39.4wt%
MgO	1.96 - 17.4wt%
P_2O_5	0.82 - 7.8wt%
B_2O_3	0 - 1.95wt%
Al_2O_3	<1wt%

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/GB 97/01667

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 22251 A (SAINT GOBAIN ISOVER ;HOLSTEIN WOLFGANG (DE); LOHE PETER (DE); SCHW) 11 November 1993 see page 1, line 37 - page 3, line 36; example 6 ---	1-3,5-7, 9
X	WO 89 12032 A (MANVILLE SALES CORP) 14 December 1989 see page 9, paragraph 3 - page 10, paragraph 2; examples 164,166-170 ---	1-3,6,7
X	DE 44 17 230 A (GRUENZWEIG & HARTMANN) 23 November 1995 see example 2 --- -/--	1,2,6

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 September 1997	30.09.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Van Bommel, L

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 93 15028 A (MORGAN CRUCIBLE CO) 5 August 1993 cited in the application see page 7, paragraph 4 - page 9, paragraph 3; examples	6,7
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